Nondestructive Evaluation of Ceramics

Edited by

Christopher H. Schilling
Joseph N. Gray

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Iowa State University

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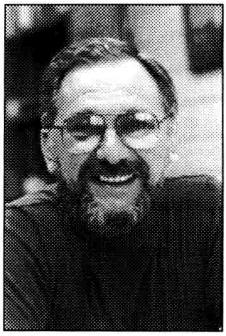
Dedication

Honoring Otto Buck



Dr. Otto Buck
(May 14, 1933–November 20, 1997)

Born on May 14, 1933, in Stuttgart, Germany, Otto Buck received his bachelor's and master's degrees in Physics from the University of Stuttgart in 1956 and 1959. He then received a doctorate in metal physics from the Max-Planck-Institut for Metallforschung in 1961. After receiving his Ph.D., he was a Research Assistant at the University of Stuttgart for three years and a Member of the Technical Staff at Siemens A.G., in Munich, Germany for two years. He then embarked on a successful, twelve-year career at the Rockwell International Science Center, where he advanced to the position of Group Manager and Principal Scientist. In 1980, he became a Professor of Materials Science and Engineering at Iowa State University and a Senior Scientist at the Ames Laboratory of the U.S. Department of Energy.

Otto Buck made pioneering scientific contributions in the areas of (a) ultrasonic measurements of internal stress and crystallographic texture, and (b) ultrasonic scattering and harmonic generation by fatigue cracks to provide information on crack tip shielding and its influence on crack growth rate and detectability. He published several, special topic journals and books on nondestructive evaluation and fracture mechanics of materials. While at Iowa State University, he became one of the founding fathers of the NSF Center for Nondestructive Evaluation. He was a member of several scientific and engineering societies, a fellow of the American Society of Metals, and a member of the editorial board of the Journal of Nondestructive Evaluation. On November 20, 1997, he died after an extended illness.

While his technical contributions are generally well recognized, perhaps less known is his impact in advancing the careers of the many people who worked under him, particularly the editors of this volume. We'll ever be grateful for his encouragement to pursue research in nondestructive evaluation of ceramic powder systems. Thank you, Otto.

C. H. Schilling
J. N. Gray

Preface

Facing stiff competition, ceramic manufacturers are currently seeking affordable, online methods of detecting and regulating production defects such as cracks, warpage, and spatial variations of porosity and composition. Breakthroughs in defect sensing technology are needed to increase the efficiency of existing production operations and also to open up new markets for ceramic products that are impossible to fabricate using traditional methods for quality control.

The objective of this volume is to present a collection of papers on recent advances in the nondestructive evaluation (NDE) of ceramics from participants at the Symposium on Nondestructive Evaluation of Ceramics held at the 99th Annual Meeting of The American Ceramic Society on May 5–7, 1997, in Cincinnati, Ohio. The goal of the symposium was to bring together researchers and industrial colleagues from the NDE and ceramic manufacturing communities to discuss needs and opportunities for NDE in the production of ceramics. This proceedings is third in a series of American Ceramic Society symposia proceedings on NDE of ceramics; these earlier symposia were held on August 25–27, 1987, in Boston, Massachusetts, and on July 9–12, 1990, in Columbus, Ohio.

As part of the effort to identify needs and opportunities for NDE in high volume manufacturing of ceramics, a workshop on this topic was held during the symposium. Panels composed of research and industrial leaders provided overviews in the workshop followed by lively discussions among the audience and panel members. Several of the main points from the workshop are summarized in the overview paper by Schilling and Gray in this proceedings.

The symposium organizers would like to express our appreciation to the participants of the panel discussion by recognizing each of the members: Bob R. Powell of the U.S. Automotive Materials Partnership and General Motors R&D Center, John Pollinger of Allied Signal Ceramic Components Incorporated, Edward Kraft of Kyocera Industrial Ceramics Corporation, Dennis Tracey of Saint Gobain-Norton Industrial Ceramics Incorporated, Said Jahanmir and Gabrielle Long of the National Institute of Standards and Technology, Muhammad Alim of the Ohio Brass Company, Christopher Schilling, Joseph Gray, and Bruce Thompson from the Center for Nondestructive Evaluation at Iowa State University, William Ellingson of the Argonne National Laboratory, Stewart Stock and Rosario Gerhardt of the Georgia Institute of Technology, and Cameron Hubbard of the Oak Ridge National Laboratory. We would also like to thank the workshop moderator, Arvid Pasto, of the Oak Ridge National Laboratory.

This Ceramic Transactions volume is organized by topic with collections of papers relevant to each of the following aspects of ceramic NDE: (i) an overview of needs and opportunities for NDE of ceramics, (ii) suspension and green-body characterization, (iii) analysis of sintered ceramics and composites, (iv) characterization of surfaces and films, and (v) advanced characterization techniques.

Any undertaking of this nature requires the combined effort of many individuals and organizations. The editors are grateful for the sponsorship of the symposium by the Basic Science, Engineering Ceramics, Whitewares, and Electronic Ceramic divisions of the American Ceramic Society. We are also grateful to the Metallurgy and Ceramics Division of the Ames Laboratory of the U.S. Department of Energy, the Department of Materials Science and Engineering at Iowa State University, the Department of Mechanical Engineering at Iowa State University, and the Center for Nondestructive Evaluation at Iowa State University for financial support in organizing the symposium. We are also grateful for the many individuals who contributed their time and expertise as reviewers of the manuscripts, and would like to recognize the authors of each manuscript for the excellent quality of each submitted document. Finally, we would like to thank Sarah Godby, Jackie Davis, Mary Cassells, and other members of the publications department of The American Ceramic Society for their patience and support during the review and editing process. We also wish to thank the other symposium organizers for their assistance: Thomas Watkins of the Oak Ridge National Laboratory and Rosario Gerhardt of the School of Materials Science and Engineering at the Georgia Institute of Technology.

It is the sincere hope of the editors that the readers of this volume will find it informative and useful in their educational, research, and manufacturing endeavors.

Christopher H. Schilling
Joseph N. Gray

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NEEDS AND OPPORTUNITIES FOR NDE IN CERAMIC PROCESSING

C. H. Schilling[1,2] and J. N. Gray[2,3]

[1] Ames Laboratory[+] and Department of Materials Science and Engineering
Iowa State University, Ames, Iowa 50010

[2] Center for Nondestructive Evaluation
Iowa State University, Ames, Iowa 50010

[3] Department of Mechanical Engineering
Iowa State University, Ames, Iowa 50010

Abstract

Post-fire defects in ceramics (e.g., cracks and warpage) can usually be traced to microstructure heterogeneities in the green state, e.g., isolated pores, packing-density gradients, and so on. Breakthroughs are needed in the way such heterogeneities are measured and understood during manufacturing, breakthroughs that could improve production efficiency and open up new markets for ceramic products. Traditional methods of quality-control are difficult to use when attempting to optimize the many different processing variables that ordinarily affect microstructure-defect evolution in ceramic production. These methods usually involve slow and costly trial-and-error procedures that are off-line in nature. They generally do not provide enough information on the spatial- and temporal-evolution of green-microstructure defects from one unit operation to the next. In this paper, we discuss needs and opportunities for process monitoring sensors in ceramic manufacturing. We emphasize the need for a new generation of process development tools to provide a better, fundamental understanding of defect evolution during processing, tools that involve the combined use of manufacturing process simulations and NDE.

[+] Ames Laboratory is operated by Iowa State University under the contract number W-7405-eng-82 with the U.S. Department of Energy.

Green-Body Defects: A Review

Green-microstructure heterogeneities include agglomerates, impurities, spatial variations of porosity and composition, delamination, segregation of different sizes of powders and granules, and preferred orientation (texturing) of asymmetric particulates (1-6). It is well known that such heterogeneities produce nonuniform shrinkage stresses during drying, debinding, and sintering, resulting in cracks and warpage.

Microstructure defects in green-bodies can be introduced during powder synthesis, or they can form and grow during subsequent unit operations including granulation, shape-forming, drying, and debinding. Most of the published literature on the evolution and elimination of green-body defects concerns dry-powder pressing, the most common, high-volume method of nonclay-ceramic production. There are several, excellent review publications in this area (3, 4, 7 - 10). By comparison, there is less active research on green microstructure evolution in the less prevalent, slurry-based forming operations of slip casting, pressure filtration, centrifugal casting, injection molding, tape casting, and gelcasting (1, 2, 5, 6, 11 - 32).

Restrictions with Conventional Quality-Control

Traditional quality-control methods suffer from practical drawbacks that prevent new breakthroughs in understanding the evolution of green-microstructure defects during ceramic manufacturing. Such methods are commonly slow, costly, and provide little information regarding the time and spatial evolution of green-microstructure heterogeneities during a given shape-forming process. Such methods usually involve trial-and-error correlations of measurements obtained well before and well after shape-forming. For example, in slip casting, measurements of the particle-size distribution, the specific surface-area, the zeta potential as a function of pH, and the viscosity as a function of shear rate are typically correlated with the green density, green strength, measurements of pore-size distribution, measurements of post-fire properties such as the density, strength, microstructure analysis, and so on. Very little information is provided regarding the effects of processing variables on the evolution of microscopic features such as particle-size segregation, packing-density gradients, the existence of flow channels in filter cakes, and so on. We should mention that fractography is a common, quality-control approach: after eliminating the biggest, strength-limiting defect by trial-and-error, the green-body strength is controlled by a smaller defect, which can then be identified by additional fractography and eliminated by more trial and error.

Another concern with traditional, quality-control methods is that they provide volume-averaged measurements of small (subcentimeter) specimen volumes, measurements that may or may not represent all other regions within a single production part or for that matter all parts on a production line. This is a serious problem for an engineer whose task is to determine, for example, if cracks in production parts should be attributed to nonuniform microstructures (e.g., density gradients occurring over several centimeters). To draw such conclusions, the engineer would be faced with a horrendous job of cutting a production part into many small pieces and then performing microscopy, density measurements, and so on, with every piece. The engineer would also face the problem of obtaining "representative" green microstructures for microscopy analysis. Because of the fragile nature of green bodies, specimen cutting usually requires the prior application of microstructure preservation techniques, such as (*i*) use of chemical fixation, or (*ii*) drying, followed by partial sintering, cutting, and polishing. Consequently, there are usually questions as to whether or not such "preservation" techniques introduce artifacts (e.g., human operator bias, polishing pull-out, changes in particle packing associated with impregnation of fixation chemicals, and so on).

Complicating the matter is the sheer number of processing variables that typically control defect evolution in ceramic greenware: (*i*) powder synthesis variables such as the particle-size and -shape distribution, powder composition and crystal structure, and changes in surface chemistry; (*ii*) granule- and slurry-processing variables such as non-uniform mixing of powder suspensions, rheological properties, pH, polymer additive concentration and composition, gravity-induced segregation; and (iii) shape-forming variables such as the properties of a slurry (e.g., composition, rheological properties, surface chemistry variables) and forming-equipment variables (e.g., the level and rate of stress application, the temperature, mold geometry). The above problems with conventional quality-control techniques make it difficult to sort through the many processing variables and determine which ones are in fact critical in a given production operation. Again, costly, trial-and-error methods are normally used for this purpose. We believe that a clearer approach for defect elimination will be possible if a better understanding of defect evolution can be established.

Market Opportunities

Building this understanding will likely provide significant opportunities to establish new markets, especially for nonclay ceramics. Consider the unprecedented variety of high-purity, nonclay ceramic powders that are just recently commercially available (33 - 38). Such powders include various borides, carbides, nitrides, and oxides for applications such as piezoelectrics, microelectronics, automotive parts, and so on. For the most part, clays generally do not meet the demanding electrical- or mechanical-properties requirements for these kinds of applications.

Despite the recent proliferation of new types of nonclay ceramic powders, there is a critical factor preventing market expansion for these raw materials: experience indicates that, compared to clays, the nonclays require much more stringent control of manufacturing process variables to remove green-microstructure heterogeneities and in turn avoid cracking during drying and debinding (5, 6). Factors that typically require more stringent control include the powder purity, particle size, slurry chemistry, mold design, and so on. Despite many years of empiricism behind the development of quality-control strategies for clay-based ceramics, these strategies often fail for nonclay ceramics. It is just recently understood that differences in interparticle friction are responsible for the remarkable difference in the fracture sensitivity of clay- versus nonclay greenware. Clays have an enhanced ability to dissipate drying and debinding stresses by particle rearrangement, a process that is inherently controlled by the stacked-platelet morphology of clays, the nature of the surface charge, and the adsorption of structured water molecules on clay surfaces (39 - 41). Nonclay ceramic powders are usually equiaxed in shape, and they do not possess the same surface chemistry necessary to reduce interparticle friction.

Consider the following trend, which is common to both clays and nonclay ceramics alike: the bigger the green body, the larger the absolute shrinkage during drying, debinding, and sintering, and the more crack-prone the body becomes during these operations. Experience indicates that, in order to prevent such cracking, larger shapes require much more stringent control of green-microstructure heterogeneities than smaller shapes. A consequence of the increased crack-susceptibility of nonclay green-bodies is that it is difficult to produce dense, engineering shapes as large as those routinely made from clay ceramics. Many years of empiricism led to the development of quality-control guidelines for clay-based ceramics, particularly meter-scale objects such as sanitaryware. However, such guidelines are not well developed for nonclay ceramics, as is evident from the scarcity of crack-free, meter-scale, dense parts that are commercially sintered from these powders (e.g., a ceramic engine block).

In order to overcome this problem, manufacturers of nonclay ceramics are faced with two alternatives: (*i*) design new chemical additives to produce more clay-like, crack-resistant greenware, or (*ii*) develop a better understanding of what the critical defects are in a given production part, how they evolve during unit operations prior to sintering, and how they can be prevented or eliminated during ceramic production. Working towards the former goal, researchers are currently developing a science base for the design of chemical additives that mediate interparticle friction and in turn produce clay-like rheological properties in suspensions of nonclay ceramic powder (14 - 16, 29, 42 - 52). However, much more research is needed before generic guidelines are perfected for the commercial development of green-strengthening additives that will allow mass production of dense, crack-free, meter-scale parts from nonclay ceramic powders.

NDE Needs & Opportunities

Let us explore option (*ii*) above: develop a better understanding of what the critical defects are in a given production part, how they evolve during unit operations prior to sintering, and how they can be prevented or eliminated during ceramic production. We believe that a combination of improved, on-line sensors integrated with a better understanding of defect evolution throughout different unit operations will help achieve this goal.

Major advances in nondestructive evaluation (NDE) equipment have been made in the past decade (see, for example, papers in this proceedings and reference 53). For example, better methods of fabricating piezoelectric sensors, semiconductor x-ray detectors, higher-performance computers, and so on, have resulted in significant improvements in measurement speed and sensitivity. In many cases, major reductions in equipment costs have also resulted. Despite these advances, on-line NDE sensors are rarely encountered in high-volume, ceramic manufacturing applications at the present time. In many cases, NDE instrumentation is too delicate and too expensive for routine use on the factory floor. If these barriers can be overcome, opportunities exist to improve manufacturing efficiency by reducing down time, energy costs, waste of ceramic raw material, and loss of value added in defective parts.

Several articles have been published on NDE of ceramics, however, most of the techniques reported are used in an off-line manner for laboratory research (see, for example, papers in this proceedings and references 5, 6, 9, 12 - 14, 17 - 19, 21 - 32, 54 - 82). We believe that significant opportunities exist to improve ceramic manufacturing efficiency if many of these NDE technologies are advanced to the point of allowing economical usage either as on-line sensors or as off-line process development tools. A critical review is needed to assess the engineering and economical barriers preventing the implementation of each NDE technology in these two respects.

We believe that the "ideal," NDE technology (or set of technologies) for on-line measurements should meet the following general requirements:

(i) It should be capable of differentiating between different types of defects, e.g., packing-density gradients, isolated pores, surface and subsurface cracks, spatial variations of composition, and so on.

(ii) It should also be capable of monitoring the time- and spatial evolution of defects throughout a succession of unit operations prior to sintering.

(iii) On-line, NDE equipment should be reliable, easy to use, and provide rapid, economical measurements without slowing production.

Specific requirements for on-line, process sensors in primary unit operations of ceramic manufacturing are summarized in Table I. Beginning with powder synthesis, traditional characterization techniques are typically off-line in nature and entail such methods as thermogravimetric analysis, pycnometry, x-ray diffraction, various types of spectroscopy, and so on. Unit operations of powder synthesis and particle-size control (e.g., sieving, milling) can benefit from the introduction of nondestructive, on-line sensors that are capable of detecting subtle variations in particle size and shape, packing-density, moisture concentration, and chemical composition. For example, improved, on-line sensors are needed to detect sporadic contaminants in powder feedstocks (e.g, dust). Another example is the need for a robust, on-line technique for morphology analysis, a method that can quickly yield numerical indices of morphic features (e.g., elongation, roughness) of powders and agglomerates. A rigorous mathematical basis for this type of analysis was recently developed (83, 84). A commercial, laboratory instrument was recently introduced that applies these mathematics to optical microscopy images, a technique that has significant potential for on-line characterization and process control (85).

On-line sensors are also needed to detect changes in the chemistry, density, and rheological properties of feedstock suspensions that are used to spray- or freeze-dry granules. For example, one can envision a system to detect changes in slurry density and solids concentration using ultrasonic sensors or even a simple, gravimetric sampling device (pycnometry). On-line sensors for colloidal chemistry parameters such as the zeta potential, electrical conductivity, chemical composition, and so on would also be useful. In addition, on-line sensors of rheological properties are needed; methods involving oscillatory tube flow (85) and torsional waveguide analysis (87) appear to have significant potential in this regard.

Improved, on-line techniques for characterizing granule properties are also needed, properties such as the moisture concentration, mass density, porosity, granule size-distribution, and morphological features such as the granule shape,

Table I. Summary of NDE Needs in Ceramic Manufacturing.

UNIT OPERATION	ON-LINE SENSORS NEEDED
• Powder Synthesis & Sizing	• Particle Shape, Size, Chemistry • Bulk Density • Sporadic Contamination of Powder
• Granulation	• Slurry Chemistry & Rheology • Granule Morphology, Size • Size Segregation of Granules • Segregation of Powders within Granules • Moisture Concentration • Flow Properties of Granules • Bulk Density
• Powder & Granule Pressing	• Microstructure Evolution & Uniformity • Porosity Mapping • Powder Composition Mapping • Moisture Concentration Mapping • Binder Concentration Mapping • Bulk Density
• Slurry Casting and Plastic Molding	• Slurry Chemistry & Rheology • Microstructure Evolution & Uniformity • Porosity Mapping • Composition Mapping • Warpage & Cracks • Bulk Density
• Drying, Debinding, and Sintering	• Microstructure Evolution & Uniformity • Moisture Mapping • Porosity Mapping • Composition Mapping • Warpage & Cracks
• Machining	• Surface & Subsurface Crack Detection • Grain Dislodging

the presence of hollow granules, and the segregation of granule constituents including binders, different types of powders or different-sized powders within a granule. Three methods of moisture and carbon-analysis are recently introduced that appear to have significant potential for on-line measurements in ceramic manufacturing: near infra-red reflectance (88, 89), nuclear magnetic resonance spectroscopy (90), and microwave spectroscopy (91).

Maintaining consistency of granule compaction and flow behavior is a key problem for many manufacturers. Traditional methods of flow-behavior characterization are typically off-line in nature (e.g., angle-of-repose, direct shear tester, compaction measurements, and so on) (10, 92, 93). On-line methods are needed which can directly measure compaction and flow properties of powders and granules. Often it is poorly understood which processing variables are critical in this respect. The ceramic industry would benefit from having a better, fundamental understanding of how granule compaction and flow behavior are controlled by critical factors such as the granule shape, microstructure, moisture concentration, and so on. It is also important to develop a better understanding of the effects of critical processing parameters on the evolution of granule shape and microstructure during spray- and freeze-drying. To achieve this goal, technology is needed that couples on-line, NDE measurements with computerized models of microstructure evolution during granule synthesis.

On-line sensors are needed that provide mapping / diagnostics of the following defects during dry pressing: packing-density gradients, local variations in the structures of pores and agglomerates, composition gradients, binder- and moisture distribution, preferred orientation of assymetric particles, and so on. We can make the same general statements regarding the need for on-line, nondestructive sensing / diagnostics of microstructure evolution in (*i*) the slurry-based forming operations of slip casting, gelcasting, tape casting, injection molding, and so on; and (*ii*) subsequent unit operations of drying, debinding, sintering, and machining. It is likely that different sensor technologies will be optimum for different unit operations. Integrating sensor measurements from each unit operation to the next will be needed in order to monitor / diagnose defect evolution between unit operations. In turn, this can help in the development of better measurement standards, better processing tolerances, and a better database of statistics on a given unit operation.

Concluding Statements

We have made the point several times that there are serious difficulties using traditional methods of quality control to sort through and optimize the multitudes of processing parameters affecting the evolution of green-